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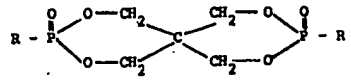
(54) FLAME RETARDANT COMPOSITION OF POLYPHENYLENE ETHER, POLYSTYRENE RESIN AND CYCLIC PHOSPHONATE

(57) Flame retardant compositions comprising a polyphenylene ether resin, a polystyrene resin and a cyclic phosphonate of formula



where R is alkyl, aryl or alkyl aryl have excellent appearance and physical properties after molding. Especially useful is diphenyl pentaerythritol diphosphonate.

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SPECIFICATION

FLAME RETARDANT COMPOSITION OF POLYPHENYLENE ETHER, POLY-STYRENE RESIN AND CYCLIC PHOSPHONATE

This invention relates to flame retardant thermoplastic compositions, and, more particularly, to compositions comprising a polyphenylene ether resin, a polystyrene resin, and a cyclic phosphonate.

Background of the Invention: Compositions comprising a polyphenylene ether resin and a polystyrene resin are well known as useful engineering thermoplastics, for molding, extrusion and the like. They are described in, for example, U.S. Patent 3,383,435.

Such compositions are normally flammable, particularly if high proportions of a polystyrene resin are present, and aromatic phosphate compounds, e.g., triphenyl phosphate, are used to retard or eliminate flammability. U.S. Patent 3,639,506, disclose that triphenyl phosphate has a tendency to reduce physical properties and describes the use of combinations of aromatic phosphates and aromatic halogen compounds to impart flame retardance, without markedly lowering resistance to distortion by heat.

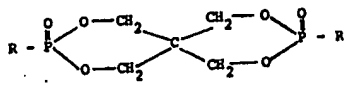
Dialkyl pentaerythritol diphosphonates have been reported in U.S. Patent 3,141,032, to be generally superior as plasticizers and as flame retardants for synthetic resins. However, it is disclosed that from 10 to 60 parts of the said phosphonate per 100 parts of resin (9.1—37.5 parts per 100 parts of the combination, by weight) is the proper amount to use, with a stated preference of 30 parts per 100 parts of resin.

It has now been discovered that cyclic phosphonate compounds by themselves are effective non-plasticizing flame retardant additives for the compositions of polyphenylene ethers and styrene resins, at an unexpectedly lower concentration. Moreover, such cyclic phosphonate materials are just as effective in flame retardance in this system as triphenyl phosphate and provide compositions with substantially the same impact resistance as the polymer composition itself.

Description of the Invention: According to this invention there are provided flame retardant compositions comprising

(a) a normally flammable composition comprising a polyphenylene ether resin and a styrene resin, and

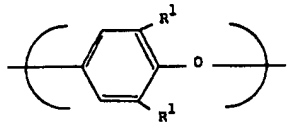
(b) an effective, flame-retardant amount of a compound of the formula



wherein

R is alkyl of from 1 to 18 carbon atoms, aryl or alkaryl.

Preferred compositions are those in which the polyphenylene ether resin is of the formula



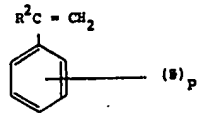
wherein

the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer equal to at least 50; and R^1, independently, is hydrogen, halogen or a mono-valent substituent free of a tertiary alpha carbon atom selected from hydrocarbon radicals, halohydrocarbon and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus and hydrocarbonoxy radicals.

Especially preferred resins are those in which R^1 is alkyl of from 1 to 6 carbon atoms, especially methyl.

Special mention is made of compositions wherein each R^1 is alkyl of from 1 to 6 carbon atoms. The component (a) can be made by those skilled in the art following the teachings of the above-mentioned Cizek patent, and the other references mentioned therein. These materials are also commercially available.

Preferred compositions also include those in which the polystyrene resin has at least 25 percent by weight units derived from a compound of the formula:



wherein

R^2 is hydrogen, alkyl of from 1 to 6 carbon atoms or halogen, Z is vinyl, halogen, or lower alkyl, and p is 0 or a whole number equal to the number of replaceable hydrogen atoms in the benzene nucleus. Preferred such polystyrene resins will be those in which p is 0 and R^2 is hydrogen. Typical styrene resins include, by way of example, homopolymers such as polystyrene and polychlorostyrene, the modified polystyrene such as rubber modified polystyrenes (high impact polystyrenes), and the styrene containing copolymers, such as the styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers, styrene/ethylene-propylene-butadiene terpolymers (EPDM), styrene maleic anhydride copolymers (SMA), styrene-acrylonitrile-alpha-alkyl styrene copolymers, styrene-acrylonitrile-butadiene terpolymers (ABS), poly-alpha-methyl styrene and copolymers of ethylvinyl benzene and divinyl benzene.

The flame retardant cyclic phosphonates will include compounds wherein R is straight a branched-chain alkyl of from about 1 to about 18 carbon atoms, e.g., methyl, ethyl, propyl, i-propyl, *n*-decyl, hexadecyl and octadecyl, aryl, e.g., phenyl, naphthyl, or alkaryl, e.g., benzyl and phenyl ethyl, containing up to 18 carbon atoms. Preferably, in the cyclic phosphonate, R will be methyl, decyl and, especially preferably phenyl.

The cyclic phosphonates can be made by those skilled in the art, e.g., by following the procedure hereinafter, or in U.S. Patent 3,141,032, for example.

The manner of adding the flame retardant component (b) to the composition (a) is not critical. Preferably, however, such component is added as part of a blend premix, the latter being passed through an extruder with extrusion temperature being maintained between 232—338°C, (450° and 640°F) depending on the composition. The strands emerging from the extruder may be cooled, chopped into pellets, molded to a desired shape.

The concentration of the flame retardant additive (b) can vary, but is dependent to a large extent on the concentration of the polystyrene resin and the particular polystyrene resin used. Lower concentrations of polystyrene resin or less flammable polystyrene resins require a lower concentration of flame retardant. Moreover, cyclic phosphonates which higher contents of phosphorous can be used in lower amounts. In general, however, amounts of from 1 to 10 parts by weight of component (b) can be used. However, to secure the major advantages, only from 2 to 10 parts per 100 parts by weight of (a) and (b) combined will be used.

Conventional additives, e.g., reinforcements, pigments, stabilizers and lubricants can also be included in conventional amounts.

Description of the Preferred Embodiments: The following examples illustrate the present invention. The flame retardant properties are determined following procedures established by the Underwriters' Laboratory Bulletin, No. 94. To meet a V—1 rating, bars measuring 6.35 cm × 1.27 cm × 0.32 cm (2—1/2" × 1/2" × 1/8") thick are twice ignited for 10 seconds each time. The compositions shall:

A. Not have any specimens which burn with flaming combustion for more than 30 seconds after each application of the test flame.

B. Not have a total flaming combustion time exceeding 250 seconds for the 10 flame applications for each set of 5 specimens.

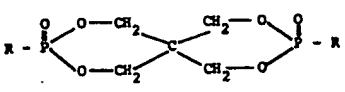
C. Not have any specimens which burn with flaming or glowing combustion up to the holding clamp.

D. Not have any specimens which drip flaming particles that ignite the dry absorbent surgical cotton located 12 inches (305 mm) below the test specimen.

E. Not have any specimens with glowing combustion which persists beyond 60 seconds after the second removal of the test flame.

EXAMPLES 1—3.

Compositions comprising polyphenylene ether resin, polystyrene resin and a cyclic phosphonate of the formula



are preblended, extruded at 277°C and chopped into molding granules. The granules are injection molded at 260°C (cylinder) and 82°C. (mold) in a 85 gm (3 oz.) Newbury injection molding machine. Physical properties and burn test results for these and for comparison examples are set forth in the Table:

TABLE

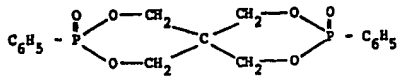
Compositions Comprising Polyphenylene Ether, Styrene Resin and Cyclic Phosphonate

Example	1	2	3	3A*	3B*
Compositions (pts. per hundred wt.)					
Poly(2,6-dimethyl-1,4-phenylene) ether[a]	35	35	35	35	35
Polystyrene resin[b]	65	65	65	65	65
Cyclic Phosphonate R=CH_3[c]	2.5	–	–	–	–
R=$C_{10}H_{21}$[d]	–	5.5	–	–	–
R=C_6H_5[e]	–	–	4.1	–	–
Triphenyl phosphate[f]	–	–	–	7.0	–
Properties					
Heat Distortion temp. at 18.7 kg/cm² (°F) °C.	(240)116	111	114	94	109
Izod impact, kg/cm (ft.-lbs./in.) notch	(4.1)22.3	–	23.4	25.0	19.6
Gardner impact, (in.-lbs.) cm.-kg	–	(90)104	196	196	127
Melt viscosity at 1,500 sec.	1630	1400	–	–	1550
UL 94 Rating	V–1	V–1	V–1	V–1	Burns

* Control
[a] PPO resin (General Electric Co.)
[b] FG 834 rubber-modified polystyrene (Foster Grant Co.)
[c] Sample from Weston Chemical Corp.
[d] See U.S. Patent 3,141,032
[e] See procedure herein
[f] Conventional, plasticizing flame retardant agent.

EXAMPLE 4.

Phenyl phosphonic dichloride, 116.95 g is added to a suspension of 40.85 g of pentaerythritol in 400 ml of acetone/triethylamine, cooled to 0—5°C. The addition is fast enough to maintain the reaction temperature below 10°C. The thick mass was stirred and allowed to warm to 25°C during 15—20 minutes, then refluxed for 13 hours, cooled, filtered and the cake was sucked dry. Then a product is obtained in 69.3% yield, m.p., after crystallization of 268—270°C. The product has an analysis corresponding to the formula:



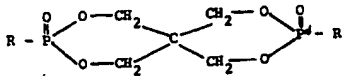
Corresponding materials can be prepared by following the procedures of U.S. Patent 3,141,032.

CLAIMS

1. A flame retardant composition comprising

(a) a normally flammable composition comprising a polyphenylene ether resin and a polystyrene resin, and

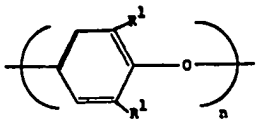
(b) a flame-retardant compound of the formula



wherein

R is alkyl of from 1 to 18 carbon atoms, aryl or alkaryl.

2. A composition as defined in claim 1 wherein said polyphenylene ether resin is of the formula



wherein

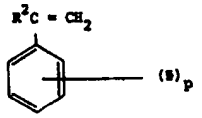
the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer equal to at least 50; and R^1, independently, is hydrogen, halogen or a mono-valent substituent free of a tertiary carbon atom selected from hydrocarbon radicals, halohydrocarbon and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus and hydrocarbonoxy radicals.

3. A composition as defined in claim 2 wherein each R^1 is alkyl of from 1 to 6 carbon atoms.

4. A composition as defined in claim 3 wherein each R^1 is methyl.

5. A composition as defined in any preceding claim wherein the polystyrene resin comprises from 20 to 80 parts by weight per 100 parts by weight of component (a).

6. A composition as defined in any claim wherein said polystyrene resin has at least 25 percent by weight of units derived from a compound of the formula:



wherein

R^2 is hydrogen, alkyl of from 1 to 6 carbon atoms or halogen; Z is vinyl, halogen or lower alkyl, and p is 0 or a whole number equal to the number of replaceable hydrogen atoms in the benzene nucleus.

7. A composition as defined in claim 6 wherein the polystyrene resin is styrene homopolymer resin.

8. A composition as defined in any preceding claim wherein, in component (b), R is methyl, decyl or phenyl.

9. A composition as defined in any preceding claim wherein the amount of component (b) is from 2 to 10 parts by weight per 100 parts by weight of (a) and (b) combined.

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